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CA-26
August 15, 1954

PREPARATION AND APPLICATION OF BROMOFORM-TRIALLYL
PHOSPHATE EMULSION FOR IMPARTING FLAME RESISTANCE
TO COTTON CLOTH ^{1/}

An aqueous emulsion of a polymer containing phosphorus and bromine has been developed for imparting flame resistance to cotton cloth. The flame resistance imparted to the cloth is retained through at least twelve launderings. Cloth treated with the emulsion retains most of its original properties and appearance and, with regard to its textile properties, appears to be suitable for use as clothing. Although the treated cloth has not been tested for an allergic or toxic reaction, extensive handling of the cloth in the laboratory has given no indications of any such reaction.

The emulsion is prepared with the polymer concentration desired in the treatment of the cloth. The concentrations required will vary with the cloth to be treated and the padding pressure to be used. Descriptions are given for the preparations of 33% and 40% polymer concentrations. For most cotton fabrics in the weight range of 8 to 9 oz. per square yard, 18-22% add-on of polymer is required for adequate flame resistance. The cloth loses some flexibility and tear resistance in treatment, but as the cloth undergoes repeated laundering, these properties approach those of the untreated cloth which has undergone an equal number of launderings. Breaking strength of the cloth is not affected by the emulsion treatment. Formation of streaks on dyed cloth during laundering is more pronounced on treated cloth than on untreated cloth. The treated cloth will not propagate a flame nor glow after exposure to flame in the standard vertical flame test^{2/} and a continuous heavy char is left.

In Tables I and II are shown the effects of the emulsion treatment on flame resistance and tear resistance of two types of cotton cloth, twill and sateen, through a series of laundry cycles. The laundry procedure was a modification of the cotton laundering procedure as described in Federal Specification CCC-T-191b, Method 5556, using an agitator-type washing machine instead of a dash wheel. This modification has been shown to correlate satisfactorily with the original procedure. Tear resistance was measured on the warp by the Elmendorf method. Flame resistance was measured by the Vertical Flame Test and is given in inches of char length. The untreated cloth burned completely in this test.

^{1/} This process is one of several flame-retarding treatments developed by the Agricultural Research Service's Southern Utilization Research Branch in cooperation with and under the sponsorship of the Office of the Quartermaster General.

^{2/} Federal Specification CCC-T-191b, Method 5902.

Table I. Tear- and Flame-Resistance of Treated Cotton Fabrics

Launderings	8.2 oz. Cotton Twill		8.5 oz. Cotton Sateen	
	Warp tear resistance (lb.) Treated ² / Untreated	Flame resistance (in.) Treated ³ / Untreated	Warp tear resistance (lb.) Treated ⁴ / Untreated	Flame resistance (in.) Treated ⁴ / Untreated
0	3.0	4.3	4.9	10.8
1	3.2	3.9	4.6	10.7
6	3.1	3.8	4.0	6.0
12	3.1	3.6	4.1	4.9

3/ 19-22% Add-on.
4/ 20-22% Add-on.

Table II. Effect of Softening Agent on Treated 8.5 oz. Cotton Sateen

Launderings	Warp tear resistance (lb.)		Flame resistance (in.)	
	Treated ⁵ / Untreated	Untreated	Treated ⁵ / Untreated	Untreated
0	6.4	10.8	5.3	5.3
1	5.6	10.7	4.8	4.8
6	4.4	6.0	5.1	5.1
12	4.2	4.9	5.2	5.2

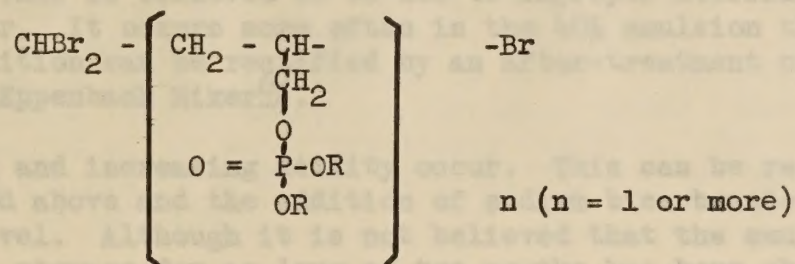
5/ 20-22% add-on of flame retardant agent followed by treatment with 4% Triton X-400⁶ solution to about a 2.5% add-on of softener.

6/ The mention of trade-names or manufacturers is not to be construed to be a recommendation by the U. S. Department of Agriculture over equivalent products or other companies.

In Table II is shown the result of softening agents on the sateen. Although the loss in strength of the treated over the untreated after twelve launderings was not serious, the high initial loss is undesirable and the use of plasticizers with the polymer has been found to be effective in reducing this loss.

Preparation of Emulsion

In the preparation of the emulsion there occurs a polymerization of triallyl phosphate together with telomerization by bromoform. The initiator of the reaction is potassium persulfate. At reaction temperature the persulphate decomposes into free radicals. Apparently, these radicals abstract a bromine atom from bromoform to yield dibromomethyl radicals. These in turn initiate a polymer chain through the allyl groups of triallyl phosphate which is terminated by the abstraction of another bromine from bromoform leaving a dibromomethyl radical which then may initiate another chain. These chains may have one or several triallyl phosphate units between the dibromomethyl group and the bromine as:



The chains are believed to be relatively short with the average value of n being between two and three.

As the reaction goes on most of the chains are crosslinked by the same type of reaction proceeding through the remaining allyl groups on the phosphate units. This leads to two types of polymers in the final emulsion, the solid crosslinked fraction, insoluble in all solvents tried, and a liquid linear fraction, soluble in most common organic solvents. Both fractions have the same phosphorus and bromine contents. Both fractions have residual unsaturation which is greater in the soluble fraction.

To be satisfactory for textile treatment, the amount of soluble polymer in the emulsion must be 17 to 33% of the insoluble polymer or 15 to 25% of the total polymer in the emulsion.

The optimum pH range for the reaction is 7.2 to 7.8. The pH of the completed emulsion should not be lower than 7.2. (Occasionally an emulsion is satisfactory if the pH drop occurs only shortly before the completion of the reaction time.) On long standing, the phosphate hydrolyzes slowly to give an acid reaction and for use in the treatment of textiles the pH of the emulsion should be adjusted to slightly above 7 with sodium bicarbonate. Sodium bicarbonate is included in the formulation to keep the pH within the desired limits.

Polyvinyl alcohol is used as the emulsifying agent. Victamul 89^{6/} may be used in addition to the polyvinyl alcohol. With 33% emulsions, the Victamul 89^{6/} gives little if any improvement. At the 40% concentration, however, the use of Victamul 89 gives a noticeable improvement in the emulsion.

Continuous stirring is necessary while the reaction is in progress. A true emulsion is not formed until the reaction is near completion. Emulsification of the monomers prior to reaction has been found to give no improvement in the properties of the final emulsion. While the rate of stirring has no noticeable effect on the properties of the 33% emulsion, violent stirring should be avoided in preparing the 40% emulsion. It may be necessary to adjust the rate of stirring when making the 40% emulsion because the liquid thickens as the reaction progresses and the stirrer should not be allowed to slow down.

Considerable caution is necessary to keep the temperature of the reaction within the limits of 80 to 85° C. The first stage of the reaction is exothermic and about 28 kilocalories of heat are liberated for each mole of triallyl phosphate used. The later stages of the reaction require the application of heat.

Occasionally the emulsion may cream during preparation and become too thick for textile treatment. This is believed to be due to improper stirring or the use of too much initiator. It occurs more often in the 40% emulsion than in the 33% emulsion. This condition can be rectified by an after-treatment of vigorous stirring as with an Eppenbach Mixer⁶.

On storage, creaming and increasing acidity occur. This can be rectified by stirring as mentioned above and the addition of sodium bicarbonate to raise the pH to the desired level. Although it is not believed that the emulsion can be stored indefinitely, storage for as long as two months has been observed and causes only slight deterioration of the flame resistant properties. High or low temperature conditions during storage do not harm the emulsion. Carbon dioxide is released slowly on storage and will build up pressure in a tightly sealed container. For this reason, provision must be made for release of such pressure.

Descriptions follow for the preparation of approximately one gallon quantities of emulsions of 33% and 40% concentrations of polymer.

33% Emulsion

Quantities of reagents:

- 837 gm. triallyl phosphate (3.8 moles)
- 583 gm. bromoform (2.3 moles)
- 568 ml. of 5% water solution of polyvinyl alcohol
- 2272 ml. water
- 107 gm. sodium bicarbonate (7.5% of weight of monomers)
- 28 gm. potassium persulfate (2.0% of weight of monomers)

The amounts of bicarbonate and persulfate are variable depending upon the quality of triallyl phosphate used. The above quantities are used with undistilled triallyl phosphate which after shaking in 20 ml. of water requires not more than one milliequivalent of standard base to neutralize 20 ml. of triallyl phosphate to the phenolphthalein end point. With distilled triallyl phosphate, containing only traces of acid or inhibitory compounds, 85 gm. (6.0%) of sodium bicarbonate and 21 gm. (1.5%) of potassium persulfate are required.

Technical bromoform has been used in place of the C. P. product and no difficulties were experienced. However, such bromoform should not contain any polymerization inhibitors.

The polyvinyl alcohol should be of medium viscosity, such as du Pont Elvanol, Grade 52-22⁶/ . The water, preferably, should be distilled or deionized.

The emulsion is prepared in a 10-12 liter, glass, round-bottomed flask, provided with a motor-driven, sealed stainless steel or glass stirrer, reflux condenser, thermometer, and inlet for adding reagents. The motor should be controlled by means of a variable transformer so that speed of stirring may be varied. The flask should be surrounded by a steam bath so arranged that it can be used alternatively with steam to heat the flask or filled with cooling water to moderate the reaction when the latter becomes vigorous.

The triallyl phosphate and bromoform are added to the flask and stirred until homogeneous. With continuous stirring, the polyvinyl alcohol solution is next added, followed by the sodium bicarbonate and all but about 250 ml. of the water. The mixture is heated as rapidly as possible to 82-83° C. (180-181°F.) with steam. The potassium persulfate is next added dry through a powder funnel and washed into the mixture with the 250 ml. of water previously reserved. The contents of the flask are then kept stirred at 80-85° C. (176-182°F.) for two hours from the time of addition of the initiator.

The first stage of the reaction, for 60 to 90 minutes after addition of the initiator, is exothermic and ordinarily requires mild cooling of the flask to keep the temperature below 85° C. This is accomplished by shutting off the steam and adding tap water to partially immerse the flask. However, care should be taken to keep the temperature above 80° C. or the reaction may slow down or even stop. In the second stage of the reaction, after 60 to 90 minutes, heat is necessary to maintain the temperature at 80-85° C.

After two hours, the reaction mixture is cooled rapidly to room temperature by adding ice water to the bath. The original heating and the final cooling are carried out as rapidly as possible to minimize hydrolysis of the phosphate.

At the end of the reaction, the pH should be 7.2 to 7.5. A pH lower than 7.0 may indicate an inferior or useless product. The soluble and insoluble polymer content may be determined as will be described below.

40% Emulsion

Quantities of reagents:

- 1308 gm. triallyl phosphate (6 moles)
- 911 gm. bromoform (3.6 moles)
- 9 gm. Victamul 89⁶/ (0.4% of weight of monomers)
- 880 ml. of 5% water solution of polyvinyl alcohol
- 2165 ml. water
- 178 gm. sodium carbonate (8% of weight of monomers)
- 56 gm. potassium persulfate (2.5% of weight of monomers)

As with the 33% emulsion, the quantities of bicarbonate and persulfate required are variable depending upon the quality of the triallyl phosphate employed. The above quantities are used with undistilled technical triallyl phosphate. With distilled material and acidity not exceeding that previously noted in the preparation of the 33% emulsion, 133 gm. (6%) sodium bicarbonate and 44 gm. (2.0%) potassium persulfate are required. It is necessary to use a relatively larger amount of initiator for the same amount of triallyl phosphate for preparation of the 40% emulsion than is required for the 33% emulsion.

The equipment and procedure are the same as with the 33% emulsion except that the Victamul 896/ is dissolved in the mixture of monomers before the polyvinyl alcohol is added. All precautions noted for the 33% emulsion apply to the preparation of the 40% emulsion. There is a greater tendency for the latter to cream during preparation and it is advisable to stir the emulsion vigorously after preparation.

The pH of this emulsion immediately after preparation should be 7.2 to 7.5. It should contain 6 to 10% soluble polymer and 26 to 33% insoluble polymer. The preparations described were carried out in a glass flask with a reflux condenser under atmospheric pressure. A stainless steel pressure vessel should be satisfactory. In this laboratory in attempts to use a stainless steel autoclave satisfactory results have not been achieved. However, the vessel used was not constructed of a high grade of stainless steel and it is believed that the metal surfaces interfered with the catalytic action of the initiator.

Determination of "Soluble" and "Insoluble" Components of Emulsion

Below are given the details for characterizing the emulsion by means of its soluble and insoluble fractions:

Duplicate 10-ml. portions of well-mixed emulsion are weighed into 50-ml. conical-tipped centrifuge tubes. The emulsion is broken by adding 10 cc. of saturated aqueous sodium chloride solution and mixing by swirling. After centrifugation for fifteen minutes at approximately 2000 r.p.m., the supernatant liquid is siphoned off gently with the aid of a pipette. Without agitating the precipitate the walls of the tube are washed with 5 cc. of distilled water, and centrifugation and siphoning are repeated as before. The wet "total polymer" is broken up with the aid of a small glass rod, and dried in the tube in a 45° C. vacuum oven for two hours. ("Drierite"6/ desiccant is used in the oven and in a drying tower through which a gentle stream of air enters the oven.)

The dried "total polymer" is extracted in the tube with 20-, 10-, and 10-cc. portions of hot Skellysolve "F"6/, allowing to stand approximately fifteen minutes after each extraction prior to each centrifugation. (If desired, the combined decanted extracts are evaporated in order to be able to isolate and weigh the non-polymeric material.)

The Skellysolve F-extracted "total polymer" is air-dried for a few minutes, and then dried for 1/2 hour at 30°-35° C. in a vacuum oven. The material is then broken up with the rod, 20 ml. of ethylene dichloride is added, and after again

breaking up lumps is allowed to stand overnight at room temperature. After centrifugation, the extract is decanted off and saved. The residue is washed with 15-, 10-, and 10-cc. portions of ethylene dichloride, allowing to stand approximately fifteen minutes after each washing prior to each centrifugation. The decanted washings are pooled with the original extract, filtered into a tared 100-ml. round-bottomed flask, and vacuum distilled, using a bubbler tube arrangement. The bubbler tube is rinsed off with a little solvent, and the flask containing the "soluble" polymer placed in an inclined position in a 40° C. vacuum oven. After bleeding a stream of air into the evacuated oven for approximately one hour to remove most of the solvent, the oven is fully evacuated and drying is continued for an additional four hours (or overnight if more feasible). The residue is weighed and reported as "soluble" polymer.

The "insoluble" polymer remaining in the centrifuge tube after ethylene dichloride extraction is broken up with the rod and dried overnight in a vacuum oven at 35°-40° C., allowing a gentle air stream to bleed into the oven. The dried material is then ground in a mortar to break up the hard lumps, returned to the centrifuge tube, and washed in the tube with 10-, 10-, and 10-ml. portions of water to remove sodium chloride and other water-solubles. After each washing, prior to centrifugation and siphoning off of the supernatants, the material is allowed to stand approximately 1/2 hour in contact with the water. The water-washed material is then broken up with the rod and dried overnight in a vacuum oven at 45°, using a gentle stream of air through a drying tower as described above, and weighed as "insoluble" polymer.

Plasticization of the Polymer

Plasticization of the polymeric finish applied to the fabric has been found to be more effective in reducing the loss in tear strength than the use of softeners previously described.

The plasticization of the polymer is accomplished by compounding the emulsion with plasticizer before treatment of the fabric. Plasticizer in the amount desired, usually from 2 to 4% of the emulsion weight, is added slowly to the emulsion with vigorous stirring which is continued for several minutes after addition of the plasticizer is complete. Treatment of the fabric with the compounded emulsion is described below.

In Table III are shown the flame and tear resistances of a fabric treated with a 33% emulsion compounded with the plasticizer Flexol TWS⁶/ (tetrabutyl thiodisuccinate) in the indicated percentage of emulsion weight. Tear resistance is notably improved and flame resistance is only slightly affected. Flexibility is improved by the use of the plasticizer.

Directions for Application of Emulsion to Cloth

Below are given the details of the application of the 40% emulsion to cloth. The 33% emulsion is applied in the same way except that the wet add-on should be about 75% instead of 60%.

Table III. Tear- and Flame-Resistance of Cotton Fabric Treated with Plasticized Emulsion

8.2 Oz. Cotton Twill					
Launderings	Warp Tear Resistance (lb.)			Flame Resistance (in.)	
	Treated*		Untreated	Treated*	
	A	B		A	B
0	3.6	3.9	4.3	5.3	5.4
1	3.8	3.8	3.9	5.4	4.9
6	3.5	3.8	3.8	5.3	5.2
12	3.3	3.6	3.6	6.1	5.8

8.5 Oz. Cotton Sateen					
Launderings	Warp Tear Resistance (lb.)			Flame Resistance (in.)	
	Treated*		Untreated	Treated*	
	B			B	
0	7.7		10.8	5.1	
1	6.7		10.7	5.4	
6	5.8		6.0	5.6	
12	4.9		4.9	6.1	

* A - Emulsion contained 2% Flexol TWS 6/

B - Emulsion contained 4% Flexol TWS

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Other Information

Any other information relative to the preparation or use of these emulsions may be obtained by addressing:

Chief, Southern Utilization Research Branch
U. S. Department of Agriculture
Southern Regional Research Laboratory
2100 Robert R. Lee Boulevard
New Orleans 19, Louisiana

Mix thoroughly. The emulsion does not coagulate, but on long standing the heavy polymeric material settles. Stirring is best accomplished with an Eppenbach⁶/ stirrer; however, any good stirrer can be used. The emulsion should be well mixed the same day that it is to be used.

Adjust pH. The pH should be adjusted to about seven with sodium bicarbonate.

Pad thoroughly onto cloth. Two dips and two nips should be used. Penetration must be very good. Pad to 60% wet add-on. 100 grams of cloth should be squeezed to 160 grams of wet weight. With 8-oz. cloth, 18-22% final add-on is required for durable flame resistance. The cloth can be run through the emulsion and the pad rolls and this process repeated again if multiple rolls are not available.

Dry and cure. Drying may be performed in a hot air oven at 80-90° C. (176 to 194°F.) for ten minutes followed by curing at 140° C. (284°F.) for six minutes. Only slightly inferior results are obtained by drying at 120° C. (248°F.) for 5 min. and curing at 140° C. (284°F.) for 6 minutes, or by drying and curing in one step at 140° C. (284°F.) for 8 minutes. During the drying and curing a small amount of fumes, presumably allyl alcohol, which are irritating to the eyes and nose are evolved. Adequate ventilation should be provided.

Wash and soften. The cloth should be washed once to remove excess chemicals. Triton X-400⁶/ should be used in the final rinse water to soften the cloth. The concentration of softener depends upon the wet pickup and should be adjusted to leave about 2.5% on the cloth.

Patent Coverage

The preparation of this emulsion and its use in rendering cotton fabrics flame-resistant is covered in U. S. Patents 2,686,768 and 2,686,769 assigned to the Secretary of Agriculture. Any correspondence relative to licensing on a royalty free, non-exclusive basis should be addressed to:

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Wash and soften. The cloth should be washed once to remove excess chemicals. Triton X-100 should be used in the final rinse water to soften the cloth. The concentration of softener depends upon the wet pickup and should be adjusted to leave about 2.5% on the cloth.

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